



Europäisches  
Patentamt  
European Patent  
Office  
Office européen  
des brevets

Description of DE10027293

[Print](#)

[Copy](#)

[Contact Us](#)

[Close](#)

## Result Page

Notice: This translation is produced by an automated process; it is intended only to make the technical content of the original document sufficiently clear in the target language. This service is not a replacement for professional translation services. The esp@cenet® Terms and Conditions of use are also applicable to the use of the translation tool and the results derived therefrom.

The instant invention concerns new powder coatings and powder coating dispersions (Pulverslurries), which contain effect pigments. The other the instant invention concerns the use of the new powder coatings and Pulverslurries in the automobile lacquer finish, the coating of buildings in the interior and outer region, the coating of furniture, doors and windows and the industrial coating, inclusive Coil coating and container coating.

Color and/or effect-giving coatings of motor vehicle bodies, in particular passenger car bodies, today preferably consist of several paint layers, which become applied one above the other and different properties to exhibit.

For example successively an electrical deposited electrical dipping lacquer finish (ETL) becomes applied as primer, a filler lacquer finish or a stone guards priming, a basis lacquer finish and a clear lacquer finish on a substrate. Here the ETL serves in particular the Korosionsschutz of the sheet. It becomes referred of the professional world frequent also as primer. The filler lacquer finish serves the cover of unevenness of the ground and grants due to its elasticity the falling rocks stability. If necessary the filler lacquer finish can serve the coating still for the reinforcement of the coverage property and for the depression of the colour. The basis lacquer finish contributes the colors and/or the optical effects. The clear lacquer finish serves the reinforcement of the optical effects and the protection of the coating before mechanical and chemical damage. Basis lacquer finish and clear lacquer finish become frequent also in summary referred as post primer. Complementary one is referred still to Römpp lexicon of paints and inks, George Thieme publishing house, Stuttgart, New York, 1998, sides of 49 and 51, "automobile lacquers".

It is therefore an important object of the modern automobile lacquer finish to reduce the amount of the amount at organic solvents significant, set free with the coating, not to even bring if on zero. Corresponding paints, like ETL, aqueous fillers or aqueous clear coats, powder coatings or Pulverslurry clear coats, are available. Adverse one however still is that for the basis lacquer finishes still non aqueous, D. h. conventional, basecoats or water basis lacquers with a comparison-white high proportion at organic solvents used to become to have, in order to disperse the pigments stable and to secure a good course of the applied layers.

\_ in addition must with the common application the paint, in particular the basecoat and clear coat, in frame the production a color and/or give coating their property very much fine one on the other tuned become, in order for example a break in the not cured layer with the application of method avoid and/or the cracking, the formation of cooker and/or the Delamination of layer prevent.



top

It would be desirable therefore, the conventional and known basecoats and water basis lacquers by solvent-free powder coatings and Pulverslurries, the effect pigments (see. Römpp lexicon of paints and inks, George Thieme publishing house, 1998, sides 176, >> effect pigments<< and sides of 380 and 381 >> metallic oxide mica pigments<< until >> Metallpigmente<<) contain to replace. First approaches for this are already present.

Thus for example out coating partners, The of magazines OF BASF, Powder of coating Special, 1/2000, sides 4 to 6, or the company publication come out powder coatings pigmented by BASF of coating AG of "powder coatings, powder coatings for industrial applications", January 2000, which come also as basecoats into considerations.

Furthermore comes out from the Japanese patent application JP 53,109,540 A1 (Derwent paper 78800A/44) a coating with 10 to 45  $\mu\text{m}$  thick a basis lacquer finish, prepared from not a pigmented Pulverslurry spezifizierten more near and 30 to 70  $\mu\text{m}$  thick a clear lacquer finish.

From the German Patent Laid open DE 27 10 421 A1 is metal effect pigments a contained Pulverslurry on the basis of amine-neutralized acrylate copolymers and melamine resins or of polyesters and epoxy resins known. The production of the pigmented Pulverslurries requires however the neutralization of the water-soluble amine-neutralized starting products with hydrochloric acid. Thereby however the metal effect pigments can become lastingly damaged. The known Pulverslurry supplies smooth, glossy, metallic coatings. It is not known whether it is suitable for the production of effect-giving multi-layer lacquer finishes.

From the Japanese patent application JP 02,014,776 a2 is a multi-layer lacquer finish made of basis lacquer finish and clear lacquer finish known, whose basis lacquer finish becomes from a pigmented Pulverslurry on the basis of hydroxygruppenhaltiger acrylate copolymers and blocked polyisocyanates prepared.

From the American patent specification US 5.379.947 A1 are cosolvensfreie pigmented and unpigmentierte Pulverslurries on the basis of for example hydroxygruppenhaltigen acrylate copolymers and blocked polyisocyanates or glycidylgruppenhaltigen acrylate copolymers and Dodecandisäure known.

Furthermore 4.268.542 A1 comparable, Effektpigmente are contained powder coatings and Pulverslurries known from the American patent specification US.

The known pigmented powder coatings and Pulverslurries exhibit meanwhile Metalleffekte and/or optical effects,

which the elevated Ansprüche of the automobile series lacquer finish, in particular in the range of the upper class, to become not yet fair to be able, why itself the powder coatings and Pulverslurries not yet when basecoats interspersed. In addition the known are inclined, with aluminum effect pigments pigmented Pulverslurries with longer storage, in particular in the warm one, to the decomposition and hydrogen development.

Object of the instant invention is it to already-set effect pigments of contained new powder coatings and Pulverslurries which do not exhibit the disadvantages of the state of the art any longer, but the multi-layer lacquer finishes with Metalliceffekten and/or dichroic effects, effect-giving in their use as basecoats, supply, which are sufficient also for the elevated claims of the car manufacturers and the customers in the segment of the upper class. In addition the new Pulverslurries is not to show decomposition and hydrogen development with the storage more.

The new powder coatings and powder coating dispersions (Pulverslurries) were found, contained accordingly at least one effect pigment, which is coated with at least an oligomer and/or a polymer, which become in the following referred as "powder coatings and Pulverslurries according to invention".

Other subject-matters according to invention come out from the description.

Regarding the state of the art it was not foreseeable surprising and for the person skilled in the art that the Pulverslurries and powder coatings according to invention permit the production of effect-giving multi-layer lacquer finishes, which are sufficient for also elevated claims of the market, whereby those particularly surprised even distribution of the effect pigments in that matrix of the coating. In addition it was surprising that the Pulverslurries according to invention no decomposition and hydrogen development shown,

Still more surprised that the Pulverslurries according to invention permits the production so called combination effect layers, which have the function of filler lacquer finishes and stone guards primings and of basis lacquer finishes in effect-giving multi-layer lacquer finishes both. This is all the more surprising than only to the Pulverslurries always for the production of paint layers with essentially a function a proposed and on the other hand the conventional and known filler lacquer finishes and basis lacquer finishes from coating materials prepared will become, which are materially very different and very particular adapted to their respective use.

In the frame of the instant invention those covers term "effect-giving multi-layer lacquer finish" both unbunte (see. see. Römp lexicon of paints and inks, George Thieme publishing house, 1998, side 590, "Unbuntpunkt") and multicolored, D. h. colored multi-layer lacquer finishes.

The Pulverslurry according to invention contains at least a finely divided dimension-stable component, D. h. a powder coating according to invention, as disperse phase and aqueous Mediums as continuous phase.

The finely divided dimension-stable component or the powder coating according to invention can be very viscous solid and/or. In the frame of the instant invention it means "very viscous" that itself the particles the bottom conventional and known conditions of the production, which storage and the application of Pulverslurries or powder coatings essentially hold back like solid particles. Preferably the powder coating is solid.

In addition the individual particles of the finely divided component or the powder coating are dimension-stable. In frames instant invention meant "dimension-stable" that the particles essentially retain the bottom conventional and known conditions of the storage and the application of Pulverslurries and powder coatings, if at all, only slight agglomerieren disintegrates and/or into smaller particles but also the bottom influence of shear forces their to original form.

Preferably the solid content of the Pulverslurry according to invention is with 10 to 80, preferred 15 to 75, particularly preferred 20 to 70, whole particularly preferred 25 to 70 and in particular 30 to 65 Gew. - %, in each case related to the Pulverslurry according to invention.

With the powder coating according to invention the solid content is naturally with 100 Gew. - %.

Preferably the average particle size of the finely divided dimension-stable components of the Pulverslurry according to invention is about 0,8 to 40  $\mu\text{m}$ , preferred 0,8 to 20  $\mu\text{m}$ , and particularly preferred with 2 to 6  $\mu\text{m}$ . Bottom average particle size becomes the 50%-Medianwert determined according to the laser diffraction method understood, D. h., 50% of the particles have a particle diameter  $\leq$  the median value and 50% of the particles a particle diameter  $>$  the median value. General one finds the particle size of the finely divided dimensionstabilen components their upper limitation if the particles cannot run due to their size with burning any longer complete and so that the film process becomes negative affected. As upper limit 40  $\mu\text{m}$  for meaningful considered become, since starting from this particle size on a blockage of the Spülkanäle of the highly sensitive application equipments is to be counted.

Pigmented Pulverslurries with such average particle sizes exhibits a better application behavior and shows with the applied film-strong of  $> 30 \mu\text{m}$ , like them current in the automotive industry with the Erstlackierung of automobiles practiced become, surprisingly a significant smaller propensity cookers and "mudcracking" than conventional combinations of filler, basecoat and clear coat up.

The grain size distribution of the powder coatings according to invention can vary comparatively wide and depends on the respective use. Preferably the grain size distribution comparatively narrow with one much minor proportion at coarse grain (grain size above 95  $\mu\text{m}$ ) is and at purifying grain (grain size of bottom 5,0  $\mu\text{m}$ ). Particularly preferred becomes powder coatings with the grain size distribution applied described in the European patent application EP 0,666,779 A1.

Surprisingly the powder coatings according to invention essentially show the same advantages, as they become managing according to invention listed with the Pulverslurries.

The Pulverslurry according to invention and the powder coating according to invention are preferably free of organic solvents (Cosolventien). In the frame of the instant invention this means that her a remainder content of volatile solvents of  $< 2,0$  Gew. - %, preferred  $< 1,5$  Gew. - % and particularly preferred  $< 1,0$  Gew. - % have.

It is according to invention from whole particular advantage, if the remainder content lies below the detection limit by gas chromatography.

The invention-essential component of the powder coatings and Pulverslurries according to invention is at least one effect pigment, which is coated with at least an oligomer and/or a polymer.

The term of effect pigments lexicon of paints and inks, George Thieme publishing house, 1998, becomes sides 176, effect pigments, >> and << sides 380 and 381 metallic oxide of mica pigments >> on Römpp << until >> Metallpigmente << referred. As effect pigments metal panel pigments therefore come like commercial aluminium bronzes, in accordance with DE-A-36 36,183 chromated aluminium bronzes, commercial high-grade steel bronze and metalliferous and non-metallic effect pigments, like to the example perglanz and/or. Interference pigments, in considerations. Particularly preferred becomes metal effect pigments, in particular aluminum effect pigments used.

Bottom oligomers become resins understood, which contain at least 2 to 15 monomer units in their molecule. In the frame of the instant invention become bottom polymeric resins understood, which contain at least 10 monomer units in their molecule. Complementary one is referred to these terms to Römpp lexicon of paints and inks, George Thieme publishing house, Stuttgart, New York, 1998 >> << oligomers, side 425.

For the production of the coating all conventional and known oligomers or polymers suitable, those not to a damage, are in particular a Zerstetzung, which effect pigments lead.

Preferably they are optical transparent, so that they reduce the desired optical effect, in particular the Metalleffekt, not or essential or do not suppress complete. In addition they are large or complete insoluble in waters or in aqueous Mediums, which contain acidic ones or bases.

Preferred ones are to a large extent compatible it with the appended bonding agents powder coatings and Pulverslurries according to invention of the complete described in the detail or. "Compatible" means the fact that itself oligomers and polymers of the coating neither forwards while or after the cure of the powder coatings and Pulverslurries according to invention in a significant extent or a complete entmischen and to hazes or eliminations leads in such a way.

Particularly preferred becomes oligomers or polymers used, which lead to a Aufschwimmen of the coated effect pigments. According to DIN 55,945 (12/1988) referred this the enrichment of pigments at the surface of a coating material. The respective effect pigments become also referred as Leaping pigments (see. Römpp lexicon of paints and inks, George Thieme publishing house, 1998, side of 351, "Leaping pigments").

Whole particularly preferred becomes thermoplastic oligomers and polymers used, whose minimum film picture temperature of those is the appended in the detail described bonding agents adapted. In addition they are not to lead to sticking the coated effect pigments together.

In particular oligomers and polymers in the managing defined sense the free of organic solvents are.

Beyond that can contain oligomers and polymers the certain number at reactive functional groups, which embody to oligomers and polymers at the surface of the effect pigments and to other them thermal self-branched or foreign-crosslinking properties in the appended defined sense lend. Examples of suitable reactive functional groups are the appended described. Their concentration may not become meanwhile so high selected that it to a damage of the effect pigments, a solubility in aqueous Mediums or in waters and/or to a rapid fixation of the coated effect pigments with the cure of the powder coatings and Pulverslurries according to invention to lead.

Examples of suitable oligomers and polymers, which are in the layer to fulfill the managing described characteristic profile essentially or complete are linear and/or branched and/or block-like, comblike and/or random constructed polyaddition resins, polycondensation resins and/or (CO) polymers of ethylenic unsaturated monomers

Examples of suitable (CO) polymers are (Meth) acrylate (CO) polymers and/or polystyrene, Polyvinylester, Polyvinylether, Polyvinylhalogenide, Polyvinylamide, polyacrylonitriles of polyethylenes, Polypropylene, Polybutylene, polyisoprenes and/or their copolymers.

Examples of suitable polyaddition resins or polycondensation resins are polyesters, alkyds, Polylactone, polycarbonates, polyethers, epoxy resin amine adducts, polyurethanes and/or polyureae.

From these oligomers and polymers (Meth) the acrylate (CO) polymers are particularly favourable, in particular (Meth) the acrylate copolymers, why they become particularly preferred used.

The production that oligomers and polymers made after the conventional and known methods of polymer chemistry in the conventional and known apparatuses for this planned, as they become appended described.

The portion of the coating of the coated effect pigments can vary wide. The amount is downward limited by the fact that a complete coating of the Effekt pigmentoberfläche must be ensured. It is thereby limited that the optical properties coated effect pigments still by the substrate the certain must become, D upward. h. the optical properties are to still correspond to those of the uncoated effect pigments. Preferably it, related to the coated effect pigment, is about 1,0 to 25, preferred 2,0 to 22, particularly preferred 3,0 to 20, whole particularly preferred 4,0 to 18 and in particular 5,0 to 15 Gew. - %.

The average particle size - like managing defined - that coated effect pigments which can be used according to invention is preferably about 5 to 20 and in particular with 10 to 11  $\mu\text{m}$ , whereby the maximum particle size is not to exceed generally 30 and in particular 25  $\mu\text{m}$ , in order to prevent blockages of the nozzles and/or the Spülkanäle in the application devices and/or standing out the effect pigments from the basis lacquer finishes and combination effect layers according to invention.

The production that effect pigments which can be used according to invention does not exhibit methodical particularities, but made in application of the solved, molten or powdery oligomers or polymers on the effect

pigments in suitable mixing units such as fluidized bed device, Dissolver, Ultraturrax, high-speed stirrer, mill or extruder. If necessary a drying process, an other grinding and/or sifting of the coated effect pigments follows to the coating.

In a first embodiment, which is preferred according to invention, the finely divided dimension-stable components contain the total amount of the used coated effect pigments of the powder clear lacquers and Pulverslurries according to invention.

In a second embodiment, which is preferred according to invention, the finely divided dimension-stable components do not contain effect pigments of the powder clear lacquers and Pulverslurries according to invention; D. h. all used coated effect pigments are present as separate solid phase. To their particle size that applies managing saying in a general manner.

In a third embodiment, which is preferred according to invention, the finely divided dimension-stable components of the powder clear lacquers and Pulverslurries according to invention contain a part that in laws of coated effect pigments, against what the other part than separate solid phase is present. Here it can itself with the portion present in the finely divided dimension-stable components around the major amount, D. h. act around more than 50% of the used coated effect pigments. Meanwhile also less than 50% in the finely divided dimension-stable components können themselves find. Regarding the particle sizes that applies managing saying also here in a general manner.

Which variant of the powder clear lacquers and Pulverslurries according to invention the advantage becomes given, depends in particular on the nature of the coated effect pigments and/or after the method, according to invention become prepared with which the used in each case powder clear lacquers and Pulverslurries. In the many cases the first preferable embodiment offers particular advantages, why it is particularly according to invention preferred.

That content of the powder clear lacquers and Pulverslurries according to invention to that according to invention to using coated effect pigments can vary very wide and depends on the requirements of the individual case, in particular after the optical effect which can be adjusted and/or the coverage property of the used in each case coated effect pigments. Preferably that is to content because of coated effect pigments with 0,1 to 20, preferred 0.3 to 18, particularly preferred 0.5 to 16, whole particularly preferred 0.7 to 14 and in particular 0.9 to 12 Gew. - %, in each case related to the powder coating according to invention or on the solid content of the Pulverslurry according to invention.

Except that according to invention to using coated effect pigments the powder clear lacquers and Pulverslurries according to invention can contain other conventional and known color and/or effect-giving pigments.

These pigments can consist of inorganic or organic compounds. The powder coatings and Pulverslurries according to invention ensure therefore due to this variety of suitable pigments an universal employment-wide and a possible implementation of a variety particularly beautiful colours and optical effects.

Examples for suitable effect pigments are the substrates that coated effect pigments which can be used according to invention.

Examples for suitable inorganic colorgiving pigments are titanium dioxide, iron oxides and soot. Examples for suitable organic colorgiving pigments are Thioindigopigmente, Indanthren blue ones, Irgalith blue ones, Heliogen blue ones, Irgazin blue one, Palomar Blue, Cromophthal red one, Hostaperm rosa ones, Irgazin orange, Sicotrans yellow one, Sicotan yellow one, Hostaperm yellow one, Paliotan yellow one, and Heliogen green one.

Complementary one becomes on Römpp lexicon of paints and inks, George Thieme publishing house, 1998, sides 180 and 181, >>iron blue pigments<< to >>ferric oxide-black<<, sides 451 to 453, >> pigments<< to >> pigment volume contraction<<, side 563, >> Thioindigo pigments<< and side 567, >> Titandioxid-Pigmente<<, referred.

The pigments can, as managing with the effect pigments described, within and outside of which finely divided dimension-stable components of the powder coatings and Pulverslurries according to invention to be present. Regarding the particle sizes that applies managing saying also here in a general manner.

In addition the powder coatings and Pulverslurries according to invention can contain organic and inorganic fillers, which can be present like the pigments within and the dimension-stable components finely divided outside of; with the pigments the saying applies here in a general manner.

Examples more suitable more organic and inorganic fillers are chalk, calcium sulphates, barium sulfate, silicates such as talc or kaolin, silicas, oxides such as aluminium hydroxide or magnesium hydroxide or organic fillers such as textile fibers, cellulose fibers, polyethylene fibers, Polyacrylnitrilpulver, PP powders or wood flour. Complementary one is referred to Römpp lexicon of paints and inks, George Thieme publishing house, 1998, sides 250 FF. >>,<< fillers. Other examples of suitable fillers are from the German patent application DE 196 06 706 A1, gaps 8, lines 30 to 64, known. Preferably they become into that indicated amounts used there.

The pigments and fillers can be present also in ultrafine, not covering form.

The portion of the pigments, fillers and coated effect pigments at the powder coatings and Pulverslurries, according to invention which can be used according to invention, can vary very wide and depends on the requirements of the individual case, in particular after the optical effect which can be adjusted and/or the coverage property of the used in each case pigments. Preferably that is to content because of pigments, fillers and effect pigments with 1,0 to 80, preferred 2.0 to 75, particularly preferred 3.0 to 70, whole particularly preferred 4.0 to 65 and in particular 5.0 to 60 Gew. - %, in each case related to on the powder coating according to invention or on the solid content of the Pulverslurry according to invention.

The powder coatings and Pulverslurries according to invention can contain additional to that managing described pigments and/or fillers or in place of this molecular-disperse distributed organic dyes.

These molecular-disperse distributed dyes are present in the finely divided dimension-stable components of the

powder coatings according to invention.

In the Pulverslurries according to invention they can be either in the dispersed finely divided dimension-stable components or in the continuous phase of the Pulverslurries according to invention present.

They can be present meanwhile also in the dispersed finely divided dimension-stable components and in the continuous phase. Here it can itself with the portion present in the finely divided dimension-stable components around the major amount, D. h. act around more than 50% of the used organic dyes. Meanwhile also less than 50% können themselves herein find. The distribution of the organic dyes between the phases can correspond to the thermodynamic balance, which results from the solubility of the organic dyes in the phases. In addition, the distribution can lie far from the thermodynamic balance remote.

Suitable ones are all organic dyes, which in the powder coatings according to invention and Pulverslurries are in the managing described sense soluble. Good suitable is light-genuine organic dyes. Particularly good suitable is light-genuine organic dyes with a small or not present propensity for migration. The migration inclination can measure the person skilled in the art on the basis its general specialized knowledge and/or determine with the help of simple orienting preliminary tests for example in the frame of sounding attempts.

That content of the powder coatings and Pulverslurries according to invention to that molecular-disperse distributed organic dyes can vary extraordinary wide and depends mainly on the color and the Buntton, which are to become adjusted, as well as after the amount of the if necessary present pigments and/or fillers

The powder coatings and Pulverslurries according to invention can be more curable physical or thermal and/or with actinic radiation. The thermal curable powder coatings and Pulverslurries again can be self-branched or foreign-crosslinking.

In the frame of the instant invention the term "physical cure" means the cure of a layer from a coating material by filming by solvent delivery from the coating material, whereby the linkage within the coating over loop formation of the polymer molecules of the bonding agents (to the term see. Römpp lexicon of paints and inks, George Thieme publishing house, Stuttgart, New York, 1998, >> bonding agent<<, sides 73 and 74) made. Or however the filming made over the coalescence of bonding agent particles (see. Römpp lexicon of paints and inks, George Thieme publishing house, Stuttgart, New York, 1998, >> cure<<, sides 274 and 275). Usually for this no crosslinking agents are necessary. If necessary the physical cure can become by atmospheric oxygen, heat or by illuminating with actinic radiation assisted.

To be received in the frame of the instant invention the referred term "self-branched" the property of a bonding agent with itself crosslinking reactions. Prerequisite for this is that in the bonding agents both types of complementary reactive functional groups are already contained, which are necessary for a crosslinking. When foreign-crosslinking become against it such coating materials, adhesives and sealants referred, where the one type of the complementary reactive functional groups in the bonding agent, and which is present other type in a curing agent or a crosslinking agent. Complementary one is referred for this to Römpp lexicon of paints and inks, George Thieme publishing house, Stuttgart, New York, 1998 >>, << cure, sides 274 to 276, in particular side 275, down.

In the frame of the instant invention bottom actinic radiation electromagnetic radiation is, like close infrared (NIR), visible light, UV-RADIATION or x-ray, in particular UV-RADIATION, to understand and corpuscular radiation such as electron radiation.

If the thermal and the cure with actinic light become common applied with a powder coating, one speaks also of "dual Cure" and "dual Curepowder coating" and/or. "Dual CurePulverslurry".

The powder coatings and Pulverslurries according to invention contain at least one bonding agent.

The bonding agents are oligomere and polymeric resins.

It is according to invention from advantage, if the minimum film picture temperature of the bonding agents amounts to at least 0 DEG C, preferred at least 10, particularly preferred at least 15, whole particularly preferred at least 20 and in particular at least 25 DEG C. The minimum film picture temperature can become determined, as an aqueous dispersion of the bonding agent becomes by means of doctor blade and on a gradient furnace an heated applied on a glass plate drawn up or a finely divided bonding agent powder on a glass plate. The temperature, with which the powdery layer films, becomes referred as minimum film picture temperature. Complementary one is referred to Römpp lexicon of paints and inks, George Thieme publishing house, Stuttgart, New York, 1998 >>, << minimum film picture temperature, side 391.

Examples for suitable binders are random, alternate and/or block-like constructed linear and/or branched and/or comblike constructed (CO) polymers of ethylenic unsaturated monomers, or polyaddition resins and/or polycondensation resins. These terms complementary on Römpp lexicon becomes paints and inks, George Thieme publishing house, Stuttgart, New York, 1998, side 457, >> polyaddition<< and >> polyaddition resins (Polyaddukte) <<, as well as sides 463 and 464, >> polycondensates<<, >> polycondensation<< and >> polycondensation resins<<, as well as sides of 73 and 74, "bonding agents", referred.

Examples of suitable (CO) polymers are (Meth) acrylate (CO) polymers or partial soaped Polyvinylester, in particular (Meth) acrylate copolymers.

Examples of suitable polyaddition resins and/or polycondensation resins are polyesters, alkyds, polyurethanes, Polylactone, polycarbonates, polyethers, epoxy resin amine adducts, polyureae, polyamides, Polyimide, polyester polyurethanes, Polyether polyurethanes or polyester polyester polyurethane polyurethanes, in particular polyester polyurethanes.

From these bonding agents polymers particular advantages exhibit (Meth) the acrylate (CO) and become therefore particularly preferred used.

The self-branched bonding agents of the thermal curable powder coatings and Pulverslurries and the dual Curepowder coatings according to invention and - Pulverslurries contain reactive functional groups, which can be received with groups of their type or with complementary reactive functional groups crosslinking reactions. The foreign-crosslinking bonding agents contain reactive functional groups, which can be received with complementary reactive functional groups, which are present in crosslinking agents, crosslinking reactions. Examples of suitable complementary reactive functional groups using according to invention are in the subsequent revue collated. In the revue the variable R stands for a acyclischen or cyclic aliphatic, an aromatic and/or an aromatic-aliphatic (araliphatic) remainder; the variables R' and R " stand for same or various aliphatic radicals or are with one another to an aliphatic or heteroaliphatic ring linked.

Revue

Examples complementary functional groups

EMI 17.1

EMI 18.1

The selection of the respective complementary groups depends to the one on the fact that it with the production, which storage, which application and that are not received melt opens of the powder coatings and Pulverslurries according to invention undesirable reactions, in particular no premature crosslinking, and/or if necessary the cure with actinic radiation not to disturb or may inhibieren, and on the other hand thereafter in which temperature range the crosslinking is to take place.

Preferably cross-linking temperatures of 60 to 180 DEG C applied become with the powder coatings and Pulverslurries according to invention. Become therefore preferably Thio, hydroxyl, N-Methylolamino N-Alkoxyethylamino, Imino, carbamat, allophane RK and/or carboxyl groups, preferred hydroxyl or carboxyl groups, on the one hand and preferably crosslinking agents with anhydride, carboxyl, Epoxy, blocked isocyanate, urethane, methyl oil, methyl oiling ago, siloxan, carbonate, revision modification NO, hydraulic XY and/or beta hydroxyalkyl amide groups, preferred Epoxy, beta hydroxyalkyl-amide, blocked isocyanate, urethane or Alkoxyethylaminogruppen, on the other hand applied.

In case of self-branched powder coatings and Pulverslurries according to invention the bonding agents contain in particular Alkoxyethylaminogruppen of methyl oil, methyl oiling ago and/or n.

Complementary reactive functional groups, which are according to invention particularly good suitable for the use in the powder coatings and Pulverslurries, are

- Carboxyl groups on the one hand and epoxy groups and/or beta hydroxyalkyl amide groups on the other hand as well as

- Hydroxyl groups on the one hand and blocked isocyanate, urethane or Alkoxyethylaminogruppen on the other hand.

The functionality of the bonding agents concerning that managing described reactive functional groups can vary very wide and depends in particular on the crosslinking density, which one wants to obtain, and/or after the functionality of the applied in each case crosslinking agents. For example the acid value preferably lies with 10 to 100, preferred 15 to 80, particularly preferred 20 to 75, whole particularly preferred 25 to 70 and in particular 30 to 65 mg KOH/g. in case of carboxylgruppenhaltiger bonding agents. Or in case of hydroxylgruppenhaltiger bonding agents the oh number is preferably about 15 to 300, preferred 20 to 250, particularly bevorzugt 25 to 200, whole particularly preferred 30 to 150 and in particular 35 to 120 mg KOH/g. Or in case of epoxidgruppenhaltiger bonding agents the epoxy equivalent weight preferably is with 400 to 2,500, preferred 420 to 2,200, particularly preferred 430 to 2,100, whole particularly preferred 440 to 2,000 and insbesondere 440 to 1.900.

Those managing described complementary functional groups can become after the conventional and known methods of polymer chemistry into the bonding agents incorporated. This can for example by the incorporation of monomers, which happen the corresponding reactive functional groups inertial, and/or with the help of polymere-analogous reactions.

Examples of suitable olefinic unsaturated monomers with reactive functional groups are

1. Monomers, which at least one hydroxyl, revision modification NO, Alkoxyethylamino, carbamat, allophane RK or imino group per molecule inertial how

- Hydroxyalkyl esters of the acrylic acid, methacrylic acid or another alpha, beta-olefinic unsaturated carbonic acid, which are derived from an alkyl glycol, which is esterified with the acidic one, or which by conversion the alpha, beta-olefinic unsaturated carbonic acid with an alkylene oxide such as ethylene oxide or propylene oxide available are, in particular hydroxyalkyl esters of the acrylic acid, methacrylic acid, Ethacrylsäure, crotonic acid, maleic acid, fumaric acid or itaconic acid, in which the Hydroxyalkylgruppe up to 20 contains carbon atoms, like 2 - Hydroxyethyl, 2-Hydroxypropyl, 3-Hydroxypropyl, 3-Hydroxybutyl, 4 - Hydroxybutylacrylat, - methacrylat, - ethacrylat, - crotonat, - maleinat, - fumarat or - itaconat; or Hydroxycycloalkylester like 1.4 - to (hydroxymethyl) cyclohexane, Octahydro-4,7-methano-1H-indendimethanol or Methylpropandiolmonoacrylat, - monomethacrylat, - monoethacrylat, - monocrotonat, - monomaleinat, - monofumarat or - monoitaconat; Reaction products from cyclic esters, like z. B. epsilon caprolactone and this hydroxyalkyl or - cycloalkylestern;

- olefinic unsaturated alcohols such as allyl alcohol;

- Polyols such as Trimethylolpropanmono or more diallylether or Pentaerythritmono, - those or - more triallylether;

- Becomes reaction products from acrylic acid and/or methacrylic acid with the Glycidylester of one in alpha position

branched monocarboxylic acid with 5 to 18 C-atoms for each molecule, in particular a Versatic TM - acidic ones, or in place of the reaction product equivalent amount an acryl and/or a methacrylic acid, which then during or after the polymerization reaction with the Glycidylester of one in alpha position branched monocarboxylic acid with 5 to 18 C-atoms for each molecule, in particular a Versatic TM - acidic one, reacted;

- Aminoethylacrylat, Aminoethylmethacrylat, allylamine or n Methyliminoethylacrylat;
- N, N-The (methoxymethyl) aminoethylacrylat or - methacrylat or N, n (butoxymethyl) aminopropylacrylat or - methacrylat;
- (Meth) acrylic acid amides like (Meth) acrylic acid amide, N-methyl, n methyl oil, N, N-dimethylol, N-Methoxymethyl, N, N-The (methoxymethyl) -, N-Ethoxymethyl and/or N, N-The (ethoxyethyl) - (meth) acrylic acid amide;
- Allophanat Acryloyloxy or Methacryloyloxyethyl, propyl or butylcarbamate or -; other examples of suitable monomers, which Carbamatgruppen contains, become in the patent specifications US-A-3,479,328, US-A-3,674,838, US-A-4,126,747, US-A-4,279,833 or US-A-4,340,497 described;

2. Monomers, which at least an acid group per molecule inertial, how

- Acrylic acid, methacrylic acid, Ethacrylsäure, crotonic acid, maleic acid, fumaric acid or itaconic acid;
- olefinic unsaturated sulfone or phosphonic acids or their partially esterified substance;
- Maleic acid mono (meth) acryloyloxyethylester, succinic acid mono (meth) acryloyloxyethylester or Phthalsäuremono (meth) acryloyloxyethylester; or
- Vinylbenzoesäure (all isomers), alpha Methylvinylbenzoesäure. (all isomers) or Vinylbenzolsulfonsäure (all isomers).

3. Epoxy groups of contained monomers like the Glycidylester of the acrylic acid, methacrylic acid, Ethacrylsäure, crotonic acid, maleic acid, fumaric acid or itaconic acid or allyl glycidyl ether.

They become preferably the production of (Meth) acrylate copolymers, in particular from glycidylgruppenhaltigen, used.

High-functional monomers that described type become managing generally used in subordinate amounts. In the frame of the instant invention bottom subordinate amounts at high-functional monomers such amounts are to be understood, which do not lead to the crosslinking or gelation of the copolymers, in particular (Meth) the acrylate copolymers, it is, one wants targeted crosslinked polymere micro particle to manufacture.

Examples suitable monomer units to the introduction of reactive functional groups in polyesters or polyester polyurethanes are 2,2-Dimethylolethyl or - propylamin, which is blocked with a Keton, whereby the resultant Ketoximgruppe becomes again hydrolyzed after the incorporation; or compounds, which contain two hydroxyl groups or two primary and/or secondary amino group as well as at least an acid group, in particular at least a carboxyl group and/or at least a sulfonic acid group, like Dihydroxypropionsäure, Dihydroxybernsteinsäure, Dihydroxybenzoesäure, 2,2-Dimethylolessigsäure, 2,2-Dimethylolpropionsäure, 2,2-Dimethylolbuttersäure, 2,2-Dimethylolpentansäure, alpha, delta - Diaminoverlansäure, 3,4-Diaminobenzoessäure, 2,4 - Diaminotoluolsulfonsäure or 2,4-Diamino-diphenylethersulfonsäure.

An example to the introduction of reactive functional groups over polymere-analogous reactions is the conversion hydroxyl groups of contained resins with phosgene, whereby groups of chlorine formates of contained resins result, and the polymere-analogous conversion of groups of chlorine formates of contained resins with ammonia and/or primary and/or secondary amines to Carbamatgruppen contained resins. Other examples of suitable methods of this type are from the patent specifications US 4.758.632 A1, US 4.301.257 A1 or US 2.979.514 A1 known.

The bonding agents of the dual Curepowder coatings according to invention and - furthermore Pulverslurries contain in the random agent at least one, of preferably at least two, group (n) with at least one with actinic radiation activatable connection (EN) per molecule.

In the frame of the instant invention a bottom connection activatable with actinic radiation a connection becomes understood, which becomes reactive when illuminating with actinic radiation and is received with other activated connections of their type polymerization reactions and/or crosslinking reactions, which run off after radical and/or ionic mechanisms. Examples suitable connections are carbon hydrogen single connections or carbon carbon, carbon oxygen, carbon nitrogen, carbon phosphorus or carbon silicon single connections or - double bonds. From these carbon carbon double bonds are particularly favourable and become therefore whole according to invention particularly preferred used. The brevity they become more half in the following as "double bonds" referred.

Therefore preferred the according to invention group contains one double bond or two, three or four double bonds. If more than a double bond becomes used, the double bonds can be conjugated. According to invention it is meanwhile from advantage, if the double bonds isolated, each for itself terminal in particular, in which in speech standing group are present here. It is according to invention from particular advantage two, in particular one, to use double bond.

The dual Curebonding agent contains described groups activatable with actinic radiation in the random agent at least one that managing. This means that the functionality of the bonding agent in this respect integral, D. h., for example same two, three, four, five or more is, or not integral, D. h., for example same 2.1 to 10.5 or more is. Which functionality one selects, depends on the requirements, which become provided to the respective pigmented dual CurePulverslurry.

If more than a group per molecule, activatable with actinic radiation, becomes applied in the random agent, the groups are structural from each other various or from same structure.

If they are structural from each other various, this means to be derived in the frame of the instant invention that two, three, four or more, in particular however two groups used activatable with actinic radiation become, from two, three, four or more, in particular however two, monomer classes.

Examples of suitable groups are (Meth) acrylate, Ethacrylat, Crotonat, Cinnamat, Vinylether, Vinylester, Dicyclopentadienyl, Norbornenyl, Isoprenyl, Isopropenyl, allyl or Butenylgruppen; Dicyclopentadienyl, Norbornenyl, Isoprenyl, Isopropenyl, allyl or Butenylethergruppen or Dicyclopentadienyl, Norbornenyl, Isoprenyl, Isopropenyl, allyl or Butenylestergruppen, in particular however acrylate groups.

Preferably the groups over urethane, urea, allophane RK, ester, ether and/or amide groups, in particular however over ester groups, are bonded to the respective basic structures of the bonding agents. Usually this is done via conventional and known polymere-analogous reactions as for instance the reaction of sidecontinuous glycidyl groups with that managing described olefinic unsaturated monomers, which contain an acid group, of sidecontinuous hydroxyl groups with the halides this monomers, of hydroxyl groups with double bonds enhaltenden isocyanates such as Vinylisocyanat, Methacryloylisocyanat and/or 1 (1-Isocyanato-1 methyl ethyl) - 3 (1-methylethenyl) - benzene (TMI TM of the company CYTEC) or of Isocyanatgruppen with that managing described hydroxylgruppenhaltigen monomers.

Meanwhile also mixtures can become from pure thermal curable and pure bonding agents applied curable with actinic radiation in the dual Curepowder coatings.

The pure powder coatings and Pulverslurries according to invention curable with actinic radiation contain preferably pure bonding agents, which contain preferably only those managing of described curable with actinic radiation, groups activatable with actinic radiation.

The material composition of the bonding agents does not exhibit in reasons particularities, but come

- all into the US patent specification US 4.268.542 A1 or US 5.379.947 A1 and the patent applications DE 27 10 421 A1, DE 195 40 977 A1, DE 195 18 392 A1, DE 196 17 086 A1, DE 196 13 547 A1, DE 196 13 547 A1, DE 196 18 657 A1, DE 196 65 2813 A1, DE 196 17 086 A1, DE 198 14 471 A1, DE 196 13 547 A1, DE 198 41 842 A1 or DE 198 41 408 A1, not the before-published German patent applications DE 199 08 018,6 or DE 199 08 013,5 or the European patent specification EP 0,652,264 A1 described, for the use in thermal and/or with actinic radiation curable Pulverklarlack Slurries planned bonding agent,
- all in the patent applications DE 198 35 296 A1, DE 197 36 083 A1 or DE 198 41 842 A1 described bonding agents planned for the use in dual Cureclear coats or
- all in the German patent application the DE 42 22 194 A1, the product Information of the company BASF of paints + colors AG, "powder coatings", 1990, or the company publication of BASF of coating AG of "powder coatings, powder coatings for industrial applications", January, 2000 described bonding agents planned for the use in thermal curable powder clear lacquers in considerations.

Here acrylate copolymers become predominantly used with the thermal or thermal and with actinic radiation curable powder coatings and Pulverslurries (Meth).

Examples of suitable (Meth) acrylate copolymers are preferably the epoxidgruppenhaltigen (Meth) acrylate copolymers with an epoxy equivalent weight with 400 to 2,500, preferred 420 to 2,200, particularly preferred 430 to 2,100, whole particularly preferred 440 to 2,000 and in particular 440 to 1,900, a pay-middle molecular weight (gel-permeation-chromatographic using a polystyrene standard certain) of preferably 2,000 to 20,000 and in particular 3,000 to 10,000, and a glass transition temperature (TG) of preferably 30 to 80, preferred 40 to 70 and in particular 40 to 60 DEG C (measured with the help of that differential scanning calometrie (DSC), like it for the use in thermal curable Pulverklarlack Slurries in considerations come in particular (S. o.) and like them in addition in the patent specifications and patent applications EP 0,299,420 A1, DE 22 14 650 B1, DE 27 49 576 B1, US 4.091.048 A1 or US 3.781.379 A1 described become.

As additional bonding agents for the dual Curepowder coatings and - Pulverslurries or as the sole bonding agents for the pure powder coatings and Pulverslurries curable with actinic radiation come into that the European patent applications EP 0,928,800 A1, EP 0,636,669 A1, EP 0,410,242 A1, EP 0,783,534 A1, EP 0,650,978 A1, EP 0,650,979 A1, EP 0,650,985 A1, EP 0,540,884 A1, EP 0,568,967 A1, EP 0,054,505 A1 or EP 0,002,866 A1, the German patent applications DE 197 09 467 A1, DE 42 03 278 A1, DE 33 16 593 A1, DE 38 36,370 A1, DE 24 36 186 A1 or DE 20 03 579 B1, the international patent applications WHERE 97/46549 or WHERE 99/14254 or the American patent specifications US 5.824.373 A1, US 4.675.234 A1, US 4.634.602 A1, 4.424.252 A1, US 4.208.313 A1, US 4.163.810 A1, US 4.129.488 A1, US 4.064.161 A1 or US 3.974.303 A1 described, to the use in UVcurable clear coats and powder clear lacquers intended bonding agents in considerations.

Also the production of the bonding agents does not exhibit methodical particularities, but made with the help of the conventional and known methods of polymer chemistry, how they become for example into that managing listed patent specifications in the detail described.

Other examples of suitable manufacturing methods for (Meth) acrylate copolymers become in the European patent applications or EP 0,767,185 A1, the German patents DE 22 14 650 B1 or DE 27 49 576 B1 and the American patent specifications US 4.091.048 A1, US 3.781.379 A1, US 5.480.493 A1, US 5.475.073 A1 or US 5.534.598 A1 or in the standard work Houben Weyl, methods of the organic chemistry, 4. Edition, tape 14/1, sides 24 to 255, 1961, described. As reactors for the copolymerization come the conventional and known agitating boilers, agitating boiler cascades, tubular reactors, Schlaufenreaktoren or Taylorreaktoren, like them for example into the patent specifications and the patent applications DE 10 71 241 B1, EP 0,498,583 A1 or DE 198 28 742 A1 or in the article of K. Kataoka in Chemical Engineering Science, tape 50, booklet 9, 1995, sides 1409 to 1416, described become, in considerations.

The production of polyesters and alkyd resins becomes for example still in the standard work Ullmanns Encyklopädie of the technical chemistry, 3. Edition, tape 14, Urban & Schwarzenberg, Munich, Berlin, 1963, sides 80 to 89 and sides 99 to 105, as well as in the books: "Résines of Alkydes polyester" of J. Bourry, Paris, publishing house Dunod,



1952, "alkyd Resins" of C. R. Martens, Reinhold Publishing corporation, New York, 1961, as well as "alkyd Resin Technology" of T. C. Patton, Interscience Publishers, 1962, described.

The production of polyurethanes and/or acrylated polyurethanes becomes for example still in the patent applications EP 0,708,788 A1, DE 44 01 544 A1 or DE 195 34 361 A1 described.

That content of the powder coatings according to invention or the disperse phase of the Pulverslurries according to invention at bonding agents can vary very wide and depends above all on whether they are self-branched physical or thermal. In these two cases it can do preferably 20 to 99.9, preferred 25 to 99.7, particularly preferred 30 to 99.5 whole particularly preferred 35 to 99.3 and in particular 40 to 99.1 Gew. - %, in each case related to the solid content of the pigmented Pulverslurry, amount to. In the other cases (thermal or thermal and with actinic radiation curable) the Bindemittelgehalt preferably is about 10 to 80, preferred 15 to 75, particularly preferred 20 to 70, whole particularly preferred 25 to 65 and in particular 30 to 60 Gew. - %, in each case related to the powder coating according to invention or the solid content of the Pulverslurry according to invention.

The thermal or thermal and, foreign-crosslinking powder coatings and Pulverslurries according to invention curable with actinic radiation contain at least a crosslinking agent, which contains the reactive functional groups complementary to the reactive functional groups of the bonding agents. The person skilled in the art can select therefore for a given powder coating or a given Pulverslurry suitable crosslinking agents light.

Examples of suitable crosslinking agents are

- Aminoplast resins, like it for example in Römpp lexicon of paints and inks, George Thieme publishing house, 1998, side 29, >> Aminoharze<<, the text book of "lacquer additives" of Johan Bieleman, Wiley VCH, Weinheim, New York, 1998, sides 242 FF., the book "Paints, coating and solvency", second completely revised edition, Edit. D. Stoye and W. Friday, Wiley VCH, Weinheim, New York, 1998, sides 80 FF., the patent specifications US 4,710,542 A1 or EP 0,245,700 A1 as well as in the article of B. Singh and coworker "Carbamylmethylated Melamines, Novel Crosslinkers for the of coating Industry", in Advanced Organic of coating Science and Technology Series, 1991, tape 13, sides 193 to 207, described become,
- Carboxyl groups contained compounds or resins, how they become for example in the patent specification DE 196 52 813 A1 or 198 41 408 A1 described, in particular Dodecandisäure,
- Epoxy groups contained compounds or resins, like them for example in the patent specifications EP 0,299,420 A1, DE 22 14 650 B1, DE 27 49 576 B1, US 4,091,048 A1 or US 3,781,379 A1 described become,
- blocked polyisocyanates, like them for example in the patent specifications US 4,444,954 A1, DE 196 17 086 A1, DE 196 31 269 A1, EP 0,004,571 A1 or EP 0,582,051 A1 described become,
- beta hydroxyalkyl amides such as N, N, N', N' Tetrakis (2-hydroxyethyl) adipamid or N, N, N', N' Tetrakis (2-hydroxypropyl) - adipamid and/or
- Trichloroethylene (alkoxycarbonylamino) - triazine, like them in the patent specifications US 4,939,213 A 1, US 5,084,541 A1, US 5,288,865 A1 or EP 0,604,922 A1 described become.

That content of the powder coatings and Pulverslurries according to invention at the crosslinking agents can vary likewise very wide and depends on the requirements of the individual case, in particular after the number of the present reactive functional groups. Preferably it is about 1.0 to 40, preferred 2.0 to 35, particularly preferred 3.0 to 30, whole particularly preferred 4.0 to 27 and in particular 5.0 to 25 Gew. - %, in each case related to the powder coating according to invention or the solid content of the Pulverslurry according to invention.

Except that managing described coated effect pigments and bonding agents as well as if necessary that managing described pigments, fillers, dyes and/or crosslinking agents can the powder coatings and Pulverslurries according to invention still at least one additive contain. This can essentially essentially be present depending upon its physical chemical properties and/or its function in the solid finely divided components of the powder coatings and Pulverslurries according to invention or in case of the Pulverslurries according to invention in the continuous phase.

Examples of suitable additives are

- thermal curable reactive-thin like position isomers Diethyloctandiole or hydroxyl groups contained hyper+branched compounds or dendrimers like them in the German patent application DE 198 50 243 A1 described become;
- with actinic radiation curable reactive solvents, like in Römpp the lexicon of paints and inks, George Thieme publishing house, Stuttgart, New York, 1998, on side 491 the bottom keyword >> reactive solvent<< described;
- Catalysts for the crosslinking such as dibutyltin dilaurate, Lithiumdecanoat or Zinkoctoat, with amines blocked organic sulfonic acids, quaternäre ammonium compounds, amines, imidazole and Imidazolderivate like 2 - Styrylimidazol, 1-Benzyl-2-methylimidazol, 2-Methylimidazol and 2 - Butylimidazol, like it in the Belgian patent No. 756,693 described become, or Phosphonium catalysts such as Ethyltriphenylphosphoniumiodid, Ethyltriphenylphosphoniumchlorid, Ethyltriphenylphosphoniumthiocyanat, Ethyltriphenylphosphonium acetateEssigsäurekomplex, Tetrabutylphosphoniumiodid, Tetrabutylphosphoniumbromid and Tetrabutylphosphonium acetateEssigsäurekomplex, as they become for example in US patent specifications US 3,477,990 A1 or US 3,341,580 A1 described;
- thermallabile radical initiators such as organic peroxides, organic azo compounds or CC-splitting initiators such as dialkyl peroxides, Peroxocarbonsäuren, Peroxodicarbonate, peroxide esters, hydroperoxides, Ketonperoxide, Azodinitrile or Benzpinakolsilylether;
- Photo initiators, like it in Römpp chemistry lexicon, 9. extended and revised edition, George Thieme publishing house Stuttgart, Bd. 4, 1991, or in Römpp lexicon of paints and inks, George Thieme publishing house Stuttgart, 1998, sides 444 to 446, described becomes;
- Antioxidantien such as hydrazines and phosphorus compounds
- UV absorbers such as triazines and Benztriphenol;
- Light-protectives such as neck compounds, Benztriazole or Oxalanilide;

- Process means;
- Radical scavengers and polymerization inhibitors such as organic phosphites or 2,6 the third Butylphenol-derivatives;
- Slip additives;
- Defoamers;
- Emulsifiers, in particular not ionic emulsifiers like alkoxyated alkanols and polyols, phenols and alkyl phenols, anionic emulsifiers such as alkali salts or ammonium salts of alkane carbonic acids, alkane-sulfone-acidic and sulfo-acidic of alkoxyated alkanols and polyols, phenols and alkyl phenols;
- Wetting agents such as siloxanes, fluorhaltige compounds, carbonic acid half esters, phosphoric acid esters, polyacrylic acids and their copolymers or polyurethanes, how they become for example in the detail in the patent application DE 198 35 296 A1 described, in particular in compound with the appended described associative Verdickern on PU basis;
- Adhesion promoters such as Tricyclodecandimethanol;
- film-formed aids such as cellulose derivatives;
- Flame retardants;
- Exhaust means such as Diazadicycloundecan or benzoin;
- Water support means;
- Rieselhilfen
- rheology-controlling additives (thick), like from the patent specifications WHERE the 94/22968, EP 0,276,501 A1, EP 0,249,201 A1 or WHERE 97/12945 known; crosslinked polymere micro particle, as they are for example in the EP-A-0 008,127 disclosed; inorganic layer silicates such as aluminium magnesium silicates, sodium magnesium and sodium magnesium fluorine lithium layer silicates of the Montmorillonit type; Silicas such as Aerosil; or synthetic polymeric with ionic and/or associative acting groups such as polyvinyl alcohol, Poly (meth) acrylamide, Poly (meth) acrylic acid, polyvinyl pyrrolidone, Styrene Maleinsäureanhydrid or ethyl maleic anhydride copolymers and their derivatives or polyacrylates; or associative thickeners on PU basis, like it in Römpp lexicon of paints and inks, George Thieme publishing house, Stuttgart, New York, 1998, >>thickener<<, sides 599 to 600, and in the text book >>lacquer additives<< from Johan Bieleman, Wiley VCH, Weinheim, New York, 1998, sides 51 to 59 and 65, described become; in particular combinations of ionic and not ionic Verdickern, how they become in the patent application DE 198 41 842 A1 adjustment of a structure-viscous behavior described, or the combination of associative Verdickern on PU basis and wetting agents on PU basis, as them become in the German patent application DE 198 35 296 A1 in the detail described.

Other examples of suitable additives become in the text book "lacquer additives" by Johan Bieleman, Wiley VCH, Weinheim, New York, 1998, described. They become applied in the conventional and known amounts.

The production of the powder coatings according to invention does not exhibit methodical particularities, but made, as managing in the product information of the company BASF of paints + colors AG, "powder coatings", 1990, or the company publication of BASF of coating AG of "powder coatings, powder coatings for industrial applications", January 2000, described, by homogenizing and dispersion, for example by means of an extruder or a snail kneading machine, and a milled one that described components. After production of the powder coatings according to invention these become by other milled ones and if necessary. by visions and screens for the application or for the dispersion to purposes of the production of the Pulverslurries according to invention prepared.

Also the production of the Pulverslurries according to invention does not exhibit methodical particularities, but made after conventional and prior art methods.

In a first preferred variant the made production of the Pulverslurries according to invention from that managing described components essentially, as in the patent applications DE 195 40 977 A1, DE 195 18 392 A1, DE 196 17 086 A1, DE-A 196 13 547, DE 196 18 657 A1, DE 196 52 813 A1, DE 196 17 086 A1, DE-A-198 14,471 A1, DE 198 41 842 A1 or DE 198 41 408 A1 in the detail described, only that in the frame of the instant invention still effect pigments processes as well become. Here the powder coating according to invention becomes by wet grinding or by stirring drying milled powder coating in waters or aqueous Mediums into the Pulverslurry according to invention transferred. Particularly preferred becomes the wet grinding.

In an other preferred variant of the production of the Pulverslurries according to invention those are emulsified managing described components in an organic solvent, whereby an emulsion of the type oil in water results, from this become the organic solvent remote, whereby the emulsified droplets solidify themselves and the Pulverslurry according to invention results. If necessary. it can become still wet-milled, in order to improve the filter barness.

In a third preferred variant of the production of the Pulverslurries according to invention a liquid melt that becomes managing described components as well as the not melted effect pigments into a emulsifying device preferably bottom addition of water and stabilisers given, the obtained emulsion cooled and filtered, whereby the Pulverslurry according to invention results. In order an high mixing quality, are it essential, the mixture obtain solvent-free in the melt to be accomplished. The polymere components accordingly become fed as viscous resin melts into the dispersion aggregates.

The powder coatings and Pulverslurries according to invention serve the production of the basis lacquer finishes according to invention of the effect-giving multi-layer lacquer finishes according to invention on a substrate.

The effect-giving Mehrschichtlackierung according to invention becomes particularly in the automobile lacquer finish, which coating of buildings in the interior and outer region, which coating of furniture, doors and windows and the industrial coating, inclusive Coil coating and container coating used, whereby all come on these technical fields of conventional and known substrates from metal, plastic, glass, wood, textile one, leather, nature and cast stone, concrete, cement or composite of these materials into considerations, whereby the electrical conductive substrates are preferred.

Preferably the effect-giving multi-layer lacquer finish according to invention is producible, by one on a substrate

1. a filler on a cathodic deposited and thermal hardened electrical dipping lacquer finish or wet-in-wet on a cathodic deposited, not or only partial hardened electrical dipping varnish layer applied, according to which one
2. the resultierende filler layer for itself alone thermal or thermal and with actinic radiation or together with the electrical dipping varnish layer thermal or thermal and with actinic radiation hardens, whereby the filler lacquer finish or stone guards priming results,
3. the powder coating according to invention or the Pulverslurry according to invention on the filler lacquer finish or stone guards priming applied, whereby a powder coating layer or a Pulverslurrschicht results,
4. the powder coating layer or Pulverslurrschicht, without interlacing it complete, ventilates or dries, or - alternative - it hardens it physical or thermal more undoder with actinic radiation whereby the basis lacquer finish results,
5. at least a clear coat on the powder coating layer or Pulverslurrschicht or - alternative - on the basis lacquer finish applied, according to which one
6. the powder coating layer or Pulverslurrschicht and the clear film of varnish (EN) common thermal and/or with actinic radiation harden, or - alternative - the clear film of varnish for itself alone thermal and/or with actinic radiation hardens whereby the basis lacquer finish and the clear lacquer finish results.

Examples of suitable cathodic electrical dipping varnishes as well as if necessary. by wet in wet methods become in the Japanese patent application 1975-142501 (Japanese Patent Laid open JP 52-065534 a2, Chemical Abstracts paper No. 87: 137427) or the patent specifications US 4.375.498 A1, US 4.537.926 A1, US 4.761.212 A1, EP 0.529.335 A1, DE 41 25 459 A1, EP 0.595.186 A1, EP 0.074.634 A1, EP 0.505.445 A1, DE 42 35 778 A1, EP 0.646.420 A1, EP 0.639.660 A1, EP 0.817.648 A1, DE 195 12 017 c1, EP 0.192.113 a2, DE 41 26 476 A1 or WHERE 98/07794 described.

Examples of suitable fillers, in particular aqueous filler, which become also referred as stone guards primings or functional layers, become in the patent specifications US 4.537.926 A1, EP 0.529.335 A1, EP 0.595.186 A1, EP 0.639.660 A1, DE 44 38 504 A1, DE 43 37 961 A1, WHERE 89/10387, US 4.450.200 A1, US 4.614.683 A1 or WHERE 490/26827 described.

As clear coats all conventional and known clear coats come into considerations.

Examples of suitable clear coats are:

- thermal curable single components (1K) -, two-components (2C) - or multi-components (3K, 4K) - clear coats, like it German patent application DE 42 04 518 A1, which European patent applications EP 0.594.068 A1, EP 0.594.071 A1, EP 0.594.142 A1, EP 0.604.992 A1 or EP 0.596.460 A1 the international patent applications WHERE 94/10211, WHERE 94/10212, WHERE 94/10213, WHERE 94/22969 or WHERE 92/22615 or the American patent specifications US 5.474.811 A1, US 5.356.669 A1 or US 5.605.965 A1 described become;
- Thermal ones of curable powder clear lacquers, like them for example from the German patent application DE 42 22 194 A1 or the product information of the company BASF of paints + colors AG, "powder coatings", 1990 known are;
- Thermal ones and/or with actinic radiation of curable Pulverslurry clear coats, like them for example into the US patent specification US 4.268.542 A1 or US 5.379.947 A 1 and the patent applications DE 27 10 421 A1, DE 195 40 977 A1, DE 19 51 8 392 A1, DE 196 17 086 A1, DE 196 13 547 A1, DE 196 18 657 A1, DE 196 52 813 A1, DE 196 17 086 A1, DE 198 14 471 A1, DE 198 41 842 A1 or DE 198 41 408 A1 or the not before-published German patent applications DE 199 08 018,6 or DE 199 08 013,5 described become; or
- UVcurable clear coats and powder clear lacquers, like it for example from the European patent applications EP 0.928.800 A1, EP 0.636.669 A1, EP 0.410.242 A1, EP 0.783.534 A1, EP 0.650.978 A1, EP 0.650.979 A1, EP 0.650.985 A 1, EP 0.540.884 A1, EP 0.568.967 A1, EP 0.054.505 A1 or EP 0.002.866 A1, the German patent applications DE 197 09 467 A1, DE 42 03 278 A1, 33 16 593 A1, DE 38 36 370 A1, DE 24 36 186 A1 or DE 20 03 579 B1, the international Patent applications WHERE 97/46549 or WHERE 99/14254 or the American patent specifications US 5.824.373 A1, US 4.675.234 A1, US 4.634.602 A1, US 4.424.252 A1, US 4.208.313 A1, US 4.163.810 A1, US 4.129.488 A1, US 4.064.161 A1 or US 3.974.303 A1 come out. The other powder coatings are known, which thermal and with actinic radiation crosslinked to become to be able (see. the European patent application EP 0.844.286 A).

The resultant clear lacquer finishes can become still with a scratch-proof coating from an organic modified ceramic material, how it is the for example bottom trade name ORMOCER TM in the trade, coated.

In general mine become those coating materials in a wet layer thickness applied, which can be used according to invention that after their cure coatings with the layer thickness favourable necessary for their functions and result. In case of the electrical dipping lacquer finish they are with 5 to 40, vorzugweise 10 to 35, particularly preferred 12 to 30 and in particular 15 to 25  $\mu\text{m}$ , into cases of the filler lacquer finish, stone guards priming or functional layer lie them with 10 to 60, preferably to 12 to 55, particularly preferred 15 to 50 and in particular 18 to 45  $\mu\text{m}$ , in case of the basis lacquer finish lie them about 5 to 50, preferably 5 to 40, particularly preferred 5 to 30 and in particular 10 to 25  $\mu\text{m}$ , and in case of a clear lacquer finish they are about 10 to 100, preferably to 15 to 80, particularly preferred 20 to 75 and in particular 25 to 70  $\mu\text{m}$ . Meanwhile the functional layer can have only a layer thickness from 20 to 50% of the total coating thickness of functional layer and basis lacquer finish in the multi-layer lacquer finish according to invention.

Beyond that the Pulverslurries according to invention serves also still the production of the combination effect layers according to invention.

In the frame of the instant invention by this coatings are to be understood, those in a effect-giving multi-layer lacquer finish at least two functions satisfied. Functions of this type are in particular the protection before corrosion, the detention switching, the absorption of mechanical energy and the effect giving. The combination effect layer serves above all the absorption of mechanical energy as well as the effect giving according to invention at the same

time; it satisfied thus the functions of a filler lacquer finish or a stone guards priming and a basis lacquer finish. Preferably the combination effect layer has beyond that still corrosion protection effect and/or detention-obtaining effect.

The thickness of the combination effect layer is according to invention preferably constant within a given effect-giving multi-layer lacquer finish. In some cases it can be advisable meanwhile to arrange the thickness in the ranges of the substrate, which are more visible a mechanical action less strong exposed not at all and/or less or, thinner in order to save material.

Of course the thickness of the combination effect layer from effect-giving multi-layer lacquer finish according to invention can vary very wide to effect-giving multi-layer lacquer finish according to invention. Here for the respective individual case the optimum thickness depends in particular on the coverage property of the used pigments (see. Römpp lexicon of paints and inks, George Thieme publishing house, Stuttgart, New York, 1998, side 124, "coverage property"), the ability, to absorb mechanical energy and/or. to dissipate, the ability, to adjust the unevenness of the substrate surface and/or the applied in each case other components of the Pulverslurry. The person skilled in the art knows therefore the optimum thickness on the basis its general specialized knowledge if necessary. bottom aid of simple orienting preliminary tests determine. Preferably the thickness of the combination effect layer is about 10 to 100, preferred 15 to 90, particularly preferred 20 to 80, whole particularly preferred 25 to 70 and in particular 30 to 60  $\mu\text{m}$ , in each case related to the layer.

The production of the invention-essential combination effect layer those become managing described Pulverslurries according to invention on those managing described primed and ungrundierten substrates applied after the invention process.

The Pulverslurries according to invention comes also for the application outside of the Automobollackierung into considerations, meanwhile lies their major technical use on the mentioned field, because its particular advantages step whole particularly open here to days. With the substrates it concerns thus motor vehicle bodies, in particular passenger car bodies, as well as parts of it, as for example doors, bonnets, fender, trunk lids spoilers, Schweller or wind deflector.

These consist in particular of steel or aluminium. The metal surfaces können here primers exhibit. In case of of aluminium it can act for example around one by anodic oxidation generated oxide layer (Eloxal TM - methods). In case of of steel it concerns usually a cathodic deposited and thermal hardened electrical dipping lacquer finish. In addition, it can become a cathodic deposited electrical dipping varnish layer used, the not thermal cured, but only dried or partial cured is.

The electrical dipping lacquer finish or the electrical dipping varnish layer is then over-laminated with the Pulverslurry according to invention, which become either cured for itself alone or common with the electrical dipping varnish layer (wet in wet methods).

The resultant combination effect layer according to invention can become with at least an additional coating coated. Preferably it concerns thereby at least one that managing described clear lacquer finishes. Thereby particularly favourable effect-giving multi-layer lacquer finishes according to invention with an excellent optical general impression and a particularly high scratch resistance result.

During the coating of the combination effect layer with a clear coat the cured combination effect layer with at least one clear film of varnish can be over-laminated, according to which these alone cured for itself becomes.

In a second variant, which is preferred according to invention, those cannot be over-laminated or only partial cured pigmented Pulverslurry layer direct with at least one clear film of varnish, according to which the clear film of varnish (EN) common with the pigmented Pulverslurry layer as well as if necessary. the electrical dipping varnish layer cured becomes (wet in wet method).

The Pulverslurries according to invention can be applied with the methods known from the liquid lacquer technology. In particular they can become by means of Spritzverfahren applied. Preferably they become followed of pneumatic syringes (compressed air syringes) of the body interior applied, by electrostatic coating of the body outer parts.

The electrostatic coating can take place by means of an electrostatic spraying gap, an electrostatic spraying bell or an electrostatic spraying disk.

The other the electrostatic coating can take place via electrostatics-assisted mechanical atomization. Preferably these by electrostatic high rotation disks or high rotation bells conducted become.

Also pneumatic syringes or compressed air painting exhibits no methodical particularities, but can by hand or by conventional and known painting automats or - robots conducted become.

Complementary one becomes for this on Römpp lexicon of paints and inks, George Thieme publishing house, Stuttgart, New York, 1998, side 186: >> Electrostatic coating<<, side 187: >> Electrostatic sprayguns<<, >>electrostatic spraying<<, as well as side 165: >> Compressed air syringes<<, referred.

Preferred one becomes the application with illumination with visible light of a wavelength of over 550  $\mu\text{m}$  or bottom light exclusion conducted, if the pigmented Pulverslurries is more curable thermal and with actinic radiation. Thereby a material change or damage of the coating material which can be used according to invention and the Overspray becomes avoided.

Of course these application procedures can become also with the application additional paint layers, preferably clear films of varnish, applied, if it does not concern powder coatings, in particular around powder clear lacquers and/or the powder coatings according to invention, those after in the product information the company BASF of paints + colors AG, "powder coatings", 1990 or the company publication of BASF of coating AG of "powder coatings, powder coatings for industrial applications", January 2000, described methods processed to preferably become.

The cure of the applied electrical dipping varnish layers, filler layers, basis films of varnish, combination effect layers and clear films of varnish does not exhibit methodical particularities, but erfogt with the help of the conventional and prior art methods and apparatuses.

With the physical cure no special measures must become grasped to and for itself; meanwhile the physical cure can become through by atmospheric oxygen, heat or by illuminating with actinic radiation assisted.

The thermal cure can take place after a certain rest time or ventilating time. It can have a duration from 30 s to 2 h, preferably 1 min to 1 h and in particular 1 min to 45 min. The rest time serves for example for the course and for degassing the layers and for evaporating volatiles like if necessary still present solvents and/or waters. Ventilating can by an elevated temperature, which is not sufficient to a cure yet, and/or by a reduced air humidity accelerated become.

The thermal cure made for example by heating in a Umluftofen or illuminating with IR and/or NIR lamps. As is the case for the cure with actinic radiation also the thermal cure stepwise can take place. Favourable way the made thermal cure with temperatures from 100 to 180 DEG C.

Preferably becomes with the cure with actinic radiation a dose from 1.000 to 3.000, preferred 1.100 to 2.900, particularly preferred 1.200 to 2.800, whole particularly preferred 1.300 to 2.700 and in particular 1.400 to 2.600 mJ/cm<sup>2</sup> applied. If necessary this cure with actinic radiation of other radiation sources can become supplemented. In case of electron beams preferably bottom inert gas atmosphere one works. This can become for example by supplies of carbon dioxide and/or nitrogen direct to the surface of the Pulverslurry layer ensured. Also in case of the cure with UV-RADIATION can, in order to be avoided, bottom inert gases worked the formation from ozonospheres to.

For the cure with actinic radiation the conventional and known radiation sources and optical remedial measures become applied. Examples suitable radiation sources are flash lamps of the company VISIT, mercury high or - low pressure vapor lamps, which if necessary with lead doped is, in order to open a jet window up to 405 Nm, or electron beam sources. Their arrangement is in principle known and can the circumstances of the workpiece and the process parameter adapted become. With complicated molded workpieces, how they are provided for automobile bodies, the not direct radiation can become accessible ranges (shade ranges) like voids, rebates and other construction dependent undercut with point, small surface or Rundumstrahlern, connected with automatic moving means for illuminating voids or edges, (partial) cured.

The plants and conditions of these hardening methods become for example in R. Cross-beam, And. V. and E. B. Curing Formulations for Printing Inks, coating and Paints, SITA Technology, Academic press, London, United Kindom 1984, described.

Here the cure stepwise can take place, D. h. by multiple exposure or irradiation with actinic radiation. This can take place also alternate, D. h. that alternate with UV-RADIATION and electron radiation becomes cured.

With dual Cure thermal cure and cure with actinic radiation can become simultaneous or successively applied. If the two hardening methods become successively used, can be ended for example with the thermal cure started and with the cure with actinic radiation. In other cases it can proving than favourably to begin and hereby end with the cure with actinic radiation.

Altogether the invention processes offer to the production of the effect-giving Mehrschichtlackierungen according to invention the ecological and economic whole particularly favourable and significant possibility not only to coatings on pure aqueous basis without emission of volatile organic to carry out, but this also with a reduced number of layers. If the corresponding solvent-free clear coats become applied, this applies also to the effect-giving multi-layer lacquer finishes according to invention, which contain at least one clear lacquer finish.

According to invention the effect-giving multi-layer lacquer finishes according to invention obtained in procedure draw by one much good adhesion on the substrate, a very good intermediate layer adhesion, an excellent corrosion protection effect, a very good protective effect against falling rocks and other mechanical damages, a very good course and a very good optical general impression, in particular which depth of shade, Metallicceffekt, dichroic effect and D. O. I. (Distinctiveness OF the reflected image) concerns, out.

The corresponding coated bodies according to invention obtain therefore a particularly high aesthetic general impression and have a particularly prolonged service life.

#### Examples

##### Example 1

The production of a effect-giving multi-layer lacquer finish according to invention with the help of a Pulverslurries according to invention

For the example 1, as first in the German patent application DE 196 13 547 A1 described, a powder coating from 77,4 parts by weight of a Methacrylatcopolymerisats from methyl methacrylate, became Glycidylmethacrylat, n-butyl acrylate and styrene, 19,4 parts by weight Dodecandisäure, 2 parts by weight of a commercial UV absorber (Ciba TM CGL 1545), 1 part by weight of the commercial light-protective Tinuvin TM 123 and 0,25 parts by weight of the commercial oxidation protective agent Irgafos TM PEPQ prepared.

This powder coating became after in the German patent application the DE 196 18 657 A1, gaps 6, indicated test specification in water dispersed, so that a pigmented Pulverslurry resulted.

The table 1 gives a survey over the type and amount of the here used components. Table 1 the production of the Pulverslurry according to invention

<tb>< TABLE> Columns=2>  
<tb> Head Col 1: Component

<tb> Head Col 2: Parts by weight  
 <tb>< September> example 1  
 <tb> AL=L> Vordispersgat:  
 <tb> demineralized water< A)>< CEL AL=R> 42,00  
 <tb> disperse Aid W22< b)>< September> 1,03  
 <tb> Triton X100< C)>< September> 0,02  
 <tb>< UCB AL=L> dimethylethanolamine< September> 0,08  
 <tb> RM 8< D)>< September> 0,90  
 <tb> powder coating< September> 28,00  
 <tb> AL=L> completion:  
 <tb> demineralized water< A)>< September> 17,49  
 <tb> RM 8< D)>< September> 0,70  
 <tb> Byk 333< e)>< September> 0,05  
 <tb> Triton X100< C)>< September> 0,18  
 <tb> effect pigment< f)>< CEL AL=R> 5,00  
 <tb>< UCB AL=L CB=1 CE=2 CB=2> A) demineralized water;  
 <tb> b) Dispersing agent on PU basis of the company Daniel Products;  
 <tb> c) Defoamers of the company Union carbides;  
 <tb> d) Thick on PU basis of the company Rohm & Haas;  
 <tb> e) Process means of the company Byk chemistry;  
 <tb> f) Aluminum effect pigment PCA 9155 of the company hit a corner-hard, coated with a  
 Polymethacrylatcopolymerisat after the Dry dazzle method in the weight ratio aluminum effect pigment: Polymer =  
 89: 11.  
 <tb>< /TABLE>

Steel boards (autobody sheets), which with a conventional and known cathodic deposited and baked electrical dipping lacquer finish coated were, became with the Pulverslurry coated manual with the help of a conventional and known spraygun (pressure: 5 bar; 2 spraying courses, horizontal and vertical). The wet layer thickness became a so selected with the fact that after burning a layer thickness of 40  $\mu\text{m}$  resulted. The Pulverslurrschicht was ventilated during 10 min with 50 DEG C and over-laminated with a commercial conventional two-component clear lacquer of the company BASF of coating AG. The resultant clear film of varnish was ventilated during 10 min, according to which the Pulverslurrschicht and the clear film of varnish became during 30 min with 150 DEG C baked. The thickness of the clear lacquer finish was about 50  $\mu\text{m}$ .

The resultant coating a white excellent coverage property up. Their Metalliceffekt and flip-flop corresponded to those to full extent a corresponding pigmented basis lacquer finish. The adhesion on the primer and the intermediate layer adhesion as well as the stone guards effect were also very good after the weathering in the condensed moisture constant climate (SKK). Disturbances in the course, cooker, cracking (mudcracking) or surface structures such as orange bowl skin were not to be observed.

#### Example 2

The production of a effect-giving multi-layer lacquer finish according to invention with the help of a powder coating according to invention

For the example 2 the powder coating became 1 prepared in accordance with example, only that 5.5 parts by weight of the coated aluminum effect pigment became 1 added in accordance with the table.

For this the components of the powder coating listed in the example 1 and the coated Aliminiumeffektpigment were weighed. The beginning-large was about 5,0 kg. The components became in a Henschel Fluidmi during two minutes with 2.800 rpm homogenized. The resultant mixture became supplied after the premixture by means of an hopper an extruder (PAY FOR PR 46). The extruder was started in each case with 110 DEG C coat temperature, and the speed became a so selected that the coat temperature held itself with 60 DEG C. The outgoing extrudate became with a chill roll on 20 DEG C cooled and comminuted with a crusher chips. The chips became before-cut and milled in a pinned disc mill. The resulting powder was abgesiebt with a tumbling filter over 125  $\mu\text{m}$ .

The application of the powder coating of the example of 2 made with the help of a laboratory hand pistol with Corona-Aufladung of the type Wagner LG1 in a layer-strong from 40 to 50  $\mu\text{m}$  on steel boards, which were coated with a conventional and known cathodic deposited and baked electrical dipping lacquer finish and a conventional and known stone guards priming. The resultant powder coating layers became baked during 10-25 minutes with 160-180 DEG C.

The so obtained basis lacquer finish was over-laminated with commercial two-component a clear coat, according to which the resultant clear film of varnish became cured with 60 DEG C.

The effect-giving multi-layer lacquer finish a white very good course and optical general impression up. Altogether the same advantages became obtained, as during the effect-giving multi-layer lacquer finish of the example 1.